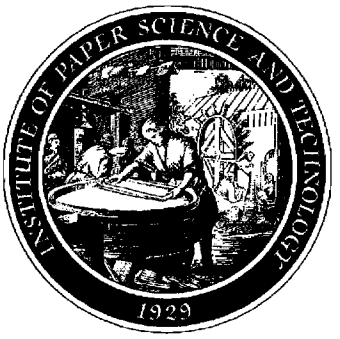

Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 951

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July 2002

Submitted to
Journal of Crystal Growth

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Synthesis of Needle-like Aragonite from Calcium Chloride and Sparingly Dissoluble Magnesium Carbonate

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Abstract

Needle-like or branch-like aragonite was prepared from sparingly dissoluble magnesium carbonate and calcium chloride aqueous solution. The morphology, particle size, and aspect ratio of the product were characterized with SEM. The polymorphs and crystal size were characterized with XRD. Comparing with calcium sulfate and sodium carbonate that were used in our previous study, a high reactant concentration region can be used to prepare needle-like aragonite when magnesium carbonate and calcium chloride aqueous solution are used. It was also found that low calcium chloride concentration is not favorable to the formation of needle-like aragonite with high aspect ratio. Magnesium ions can increase not only aragonite fraction but also aragonite crystal size. However, the change of aragonite particle aspect ratio was not marked by the addition of magnesium chloride. High synthesis temperature is favorable to both aragonite fraction and its aspect ratio. High pH is beneficial to the formation of aragonite. Aging will result in a transformation of aragonite into calcite if calcite exists in the suspension. For the suspension system without calcite and with Mg^{2+}, aging will decrease the needle length and the aspect ratio.

Key Words: Calcium carbonate, Aragonite, Morphology, Filler, PCC

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1. Introduction

Much attention has been paid to the study of needle-like calcium carbonate due to its potential advantages in the application of paper, plastics, and rubber-making as filler. Calcium carbonate has three types of polymorphs: calcite, aragonite, and vaterite. Calcite is the thermodynamics-stable phase of calcium carbonate [1,2]. Vaterite is the most unstable form [3]. Generally, aragonite calcium carbonate is liable to give needle-like or spindle-like morphology [4-6]. Controlled conditions have been widely studied in the synthesis of aragonite. These conditions include temperature [4,5,7,8], pH of the reaction solution [5,7,9,10], and supersaturation [4,5,11-13]. A lot of organic additives [13-17] were studied to improve the formation of aragonite. In order to synthesize needle-like aragonite, some inorganic additives have also been studied. Fairchild et al. [12] disclosed a technique for the preparation of acicular calcite and aragonite. This technique involves the reaction of calcium hydroxide or calcium oxide and carbon dioxide in the presence of water-soluble aluminum salt. The needle-like particle possessed a length of 1-4 microns and a diameter of 0.1-0.5 microns. However, more attention has been paid to magnesium-containing compounds [5,7,13,14,18-26]. Meldrum and Hyde [14] have studied the morphological influence of magnesium and organic additives on calcium carbonate precipitate. A molar ratio region of Ca/Mg from 0.16 to 1.29 and a ratio of Ca/Organic additive from 0.37 to 57.14 were studied. They found that magnesium promoted the formation of aragonite. As Mg inhibits the growth of crystal nuclei, a principal mechanism was thought to be through the aggregation of precritical crystalline. Addition of magnesium ions to the crystallizing solutions resulted in two effects: a much wider range of morphologies and a transition from single crystal to crystallite aggregates. Mg^{2+} ions can affect crystal morphologies by both their adsorption on specific crystal faces [13,19,20] and by altering the calcite nucleation and growth processes [21-23]. It was thought that an Mg/Ca ratio of 4 is required to induce the precipitation of aragonite rather than calcite [13]. Metable aragonite is favored when the rate of precipitating and in particular the rate of CO_3^{2-} ions supply are high [21,27]. Other research [28-31] also

indicated that in the presence of magnesium ions, the growth rate of calcite in supersaturated solution was greatly decreased while the growth of aragonite was not changed.

It is well known that both nucleation and growth of crystalline depend on supersaturation of the solution. Needle-like aragonite has to be synthesized in some given supersaturation region. High supersaturation is favorable to the formation of calcite. In our previous study [32] a series of sparingly dissoluble calcium salts were used as reactants to control supersaturation of PCC synthesis, and needle-like aragonite was synthesized.

In this study, sparingly dissoluble carbonate salts were used for synthesizing needle-like aragonite. For the system of Ca^{2+} and $MgCO_3$, the following reaction will take place:

$$Ca^{2+} + MgCO_3 = CaCO_3 + Mg^{2+}$$

The reactant constant is:

$$K = \frac{[Mg^{2+}]}{[Ca^{2+}]} = \frac{K_{SPMgCO_3}}{K_{SPCaCO_3}} = \frac{6.82\times10^{-6}}{3.36\times10^{-9}} = 2.0\times10^{3}$$

Moreover, as discussed above, the presence of product Mg^{2+} will promote the formation of aragonite. $CaCl_2$ aqueous solution and $MgCO_3$ aqueous suspension were used as reactants in this research. The purpose is to explore the difference caused by different sparingly dissoluble salts.

2. Experimental section

2.1 Synthesis of precipitate calcium carbonate

Magnesium carbonate was synthesized by mixing 1.000 L of 0.5 mol/L of $MgCl_2$ (Aldrich 98%) and 500 mL of 1.000 mol/L sodium carbonate (Aldrich, 99.5%) with magnetic agitation. After filtration the precipitate was rinsed 5 times with 100 mL of DI water. Then the precipitate was dried at 120°C for 3 h. In order to synthesize aragonite PCC, magnesium carbonate was added to DI water and then was heated to a given temperature. After agitation for 15 minutes calcium chloride (Aldrich, 99+%) solution with a different concentration was added to the

suspension at a given rate. Finally, the product suspension was filtrated without aging, rinsed three times with DI water, and dried at 120°C for 2 h. Calcium chloride was 20% excessive. For the investigation on the influence of calcium chloride concentration, 50 mL of suspension with 0.03 mol of magnesium carbonate was heated to 70°C. Then calcium chloride solution with a concentration region from 0.025 mol/L to 3.00 mol/L was added at a rate of 8 mL/min to the suspension with magnetic agitation. Here a high concentration region was studied compared with our previous study [32]. As discussed above, Mg^{2+} can promote the formation of aragonite. An increase of Mg^{2+} concentration will decrease solubility of $MgCO_3$ and thus decrease supersaturation of $CaCO_3$ in the synthesis. Therefore, the influence of Mg^{2+} concentration was studied where $MgCl_2$ solution was added as an additive to the $MgCO_3$ suspension. Then the suspension was heated to 60°C. 1.0 mol/L of $CaCl_2$ solution was added to the suspension at 0.4 mL/min under stirring. Similar conditions were used in the research on the influence of reaction temperature where $MgCl_2$ was added to the suspension to a concentration of 0.16 mol/L. The influence of Mg^{2+} on stability of aragonite and the effect of aging on aspect ratio of aragonite were studied by aging product suspension with and without $MgCl_2$ for different times. The effect of pH was also studied in a region from 9 to 11 because of the possibility that too high pH will result in the formation of $Mg(OH)_2$. 0.1mol/L ammonium chloride (Aldrich, reagent) solution and sodium hydroxide (Aldrich, 50% aqueous solution) solution were added to the suspension to different preset pH.

2.2 Characterization

A scanning microscope (JEOL, JSM-35C, Tokyo, Japan) was used to visualize morphology of the product calcium carbonate particle and to measure needle-like particle size as well as aspect ratio where the length and the largest width of more than 50 particles were used in the calculation. An average value was calculated from these data.

XRD spectra of the product were measured with a PW1800 x-ray diffractometor (Philips, USA). A step size of 0.02° and scanning speed of 0.4 S per step were used to record spectra in the region from 20° to 80° or 20° to 32°. Crystal size of aragonite and calcite were measured with an x-ray broadening method [33,34]. Peak width of $d_{(104)}$=3.3035Å, 2θ=29.404° of calcite and $d_{(111)}$=3.396Å, 2θ=26.213° of aragonite are used in the calculation. Single crystal silicon was used to calibrate broadening of the instrument. The polymorphic fraction of aragonite in crystalline calcium carbonate can be evaluated using the following equation [35] when no vaterite exists:

$$y = \frac{3.9S_a}{S_c + 3.9S_a}$$

where y is the calculated fraction of aragonite; S_c and S_a are the integrated intensities of x-ray diffraction spectra characteristic of calcite ($d_{(104)}$=3.3035Å, 2θ=29.404°) and aragonite ($d_{(111)}$=3.396Å, 2θ=26.213°), respectively.

3. Results and Discussion

3.1. Relation between supersaturation and polymorphs

Relative supersaturation of $CaCO_3$ in the synthesis can be calculated by [36]:

$$\sigma = \Omega^{1/2} - 1 = [\alpha_{Ca^{2+}}\alpha_{CO_3^{2-}} / K_{sp}]^{1/2} - 1$$

Ignoring the effect of ion strength $[CO_3^{2-}]$ in $MgCO_3$ suspension can be calculated by:

$$[CO_3^{2-}] = \frac{K_{SPMgCO_3}}{[Mg^{2+}]}$$

If no soluble magnesium salt is added the equilibrium concentration of $[CO_3^{2-}]$ is 2.612×10^{-3}

The relative supersaturation of the synthesis can be written as:

$$\sigma = [2.612\times10^{-3}[Ca^{2+}]/3.36\times10^{-9}]^{1/2} - 1$$

$$= 8.82 \times 10^2 \, [Ca^{2+}]^{1/2} - 1$$

The dependence of precipitate growth rate, R_G, on relative supersaturation, σ, can be expressed by [36]:

$$R_G = k_g \sigma^n$$

or [37]:

$$R_G = A\sigma^2 \tanh(B/\sigma)$$

Therefore, $R_G = A\sigma^2$ for low values of σ, whereas for high values $R_G = A\sigma$, where A and B are constants. So for our research the growth rate should be directly proportional to relative supersaturation. XRD spectra of both previous research [32] and this research are given in Fig. 1. No calcite was found in the sample prepared from 0.025 mol/L $CaCl_2$ and $MgCO_3$ suspensions, while some calcite can be found from the one prepared with 0.01 mol/L Na_2CO_3 solution and $CaSO_4$ suspension in our previous study [32]. The concentration of $CaCl_2$ solution is higher than that of Na_2CO_3. The polymorphs difference is more marked than that of their supersaturation, which means that product $MgCl_2$ in this synthesis promoted the formation of aragonite or retarded the formation of calcite [28-31]. The result, that aragonite appeared at a lower supersaturation than calcite, suggests that critical supersaturation for aragonite nucleation is lower than that of calcite [38]. Existence of Mg^{2+} probably increases the critical supersaturation for the formation of calcite due to its adsorption on subnuclei. Aragonite fraction of the products versus $CaCl_2$ concentration is given in Table 1. Aragonite decreased with the increase of $CaCl_2$ concentration. This tendency was similar to the previous study [32].

An SEM image of these samples is given in Fig. 2. Some branch-like structure can be found. A statistical result of the aspect ratio of these branches or needles is also given in Table 1. An increasing tendency is also shown with $CaCl_2$ concentration. The reason requires additional study.

3.2 Promotion of $MgCl_2$ on the formation of needle-like aragonite

$MgCl_2$ is a product of the synthesis reaction. With the increase of Mg^{2+} concentration, the concentration of CO_3^{2-} will decrease because of the equation below:

$$[Mg^{2+}]\times[CO_3^{2-}]=K_{SP}=6.82\times10^{-6}$$

So the supersaturation of the reaction will decrease, which should be favorable for the formation of aragonite. Moreover, Mg^{2+} was thought to retard the formation of calcite [28-31]. The ratio of $[Mg^{2+}]/[Ca^{2+}]$ in these studies, generally, is much larger than 1 [39]. Therefore, $MgCl_2$ was added as an additive in this research to promote the formation of aragonite. Aragonite fraction PCC prepared in this way is given in Fig. 3. When the concentration of added $MgCl_2$ reached 0.05 mol/L, no calcite was produced. This result suggests that $MgCl_2$ really promoted the formation of aragonite. The crystal size of the aragonite of these samples is given in Table 2. An increasing tendency was found with the increase of the $MgCl_2$ concentration. This contrasts with the results of our previous research [32] from Na_2CO_3 and $CaSO_4$ suspension, where a decreasing tendency of aragonite crystal size was observed with the increase of sulfate ion concentration. All these results suggest that counter-ions of sparingly dissoluble salt play an important role in the growth kinetics of PCC. No evident change of aspect ratio was found in the experiment error region.

3.3. Effect of reaction temperature and pH

Aragonite fraction shows an increasing tendency with the increase of reaction temperature. When the temperature rose to 70°C all PCC was aragonite. This result agrees with other research on the influence of temperature [4,5,7,8]. Generally, favorable temperature for the formation of aragonite is above 60°C. In previous research [32], we found that an optimal temperature for the formation of aragonite is around 60°C, and above that, the fraction of calcite increased. This difference should be ascribed to different sparingly dissoluble salts, i.e., their counter-ions. This

result suggests that the composition of sparingly soluble salt plays an important role to polymorphs of PCC. The aspect ratio of these needle-like or branch-like aragonites is given in Fig. 4. The SEM images are given in Fig. 5. A marked increasing tendency of aspect ratio can be found as temperature increased. These results mean that high temperature is favorable to the formation of PCC with both high aragonite fraction and high aspect ratio. Aragonite fraction prepared under different initial pH of the suspension is given in Fig. 6. It is shown that the fraction increased with pH up to pH 11. This agrees with the result of Tai et al. [4]. In our research, however, the pH cannot be too high because of the formation of $Mg(OH)_2$ precipitate.

3.4. Effect of aging on polymorphs and aspect ratio of aragonite

There are two possible reactions existing during the aging. The first one is the transformation of aragonite into calcite because calcite is the thermodynamics-stable phase of calcium carbonate [1,2]. The second is Ostward ripening [40-43] where the average size of the particle will increase with the aging time through the dissolution of small particles and growth of large particles. For a spherical particle and a highly dispersed particle system, the growth of average particle radius $\bar{r}$ is controlled by diffusion. The rate law follows the equation below:

$$\bar{r}^{3} - \bar{r}_{0}^{3} = Kt$$

where K is a rate constant. Similarly, ripening of needle-like particles should also show an increasing tendency of particle size. Two series of samples were prepared in this research. The first one was prepared without adding $MgCl_2$. The aragonite fraction, characterized with XRD, showed a decreasing tendency during the aging. A marked transformation of aragonite to calcite was found in 24 h. This transformation was the result of the growth of calcite at a cost of aragonite dissolution. The second series of samples were prepared from a suspension with $MgCl_2$ additives. XRD diffraction patterns indicated that no transformation of aragonite into calcite was observed in 98 h, which should be ascribed to the absence of calcite "seeds" in the system. This

result means that aragonite is stable enough in water suspension with Mg^{2+} if no calcite is presented. The aspect ratio of needle-like or branch-like aragonite is given in Fig. 7, and the particle size, measured with SEM, is given in Fig. 8. It is found that the aspect ratio decreases with aging time. Moreover, this tendency resulted from a marked decrease of particle length. The thickness of the particle slightly increases during the aging for 98 h at 60°C, where the end part of the needle particle with a small curvature radius dissolved because of a high equilibrium concentration C_e [43, 44] in terms of Gibbs-Thomson equation:

$$C_e = C_\infty \exp(\frac{2\sigma V_m}{rRT})$$

where C_∞ is the solubility of the solid with infinite dimensions, σ is the specific energy, R is the gas constant, and T is the absolute temperature. Similarly, some small particles also showed higher equilibrium concentration C_e and also dissolved. The center part of the needle-like particle will grow because of a larger curvature radius and lower equilibrium concentration C_e. These results indicate that aging is disadvantageous to the preparation of needle-like particles with high aspect ratio if the particle does not possess uniform thickness. Theoretically, if the particle possesses a uniform thickness, aging cannot increase aspect ratio through Ostward ripening.

4. Conclusion

Sparingly dissoluble magnesium carbonate and calcium chloride aqueous solution can be used to prepare needle-like or branch-like aragonite. Compared with the synthesis from calcium sulfate and sodium carbonate, a high reactant concentration region was available because of the promoting effect of product magnesium chloride. Low calcium chloride concentration is not favorable to the formation of needle-like aragonite with high aspect ratio. Magnesium ions increased not only aragonite fraction but also aragonite crystal size. However, the change of aragonite particle aspect ratio was not marked due to the addition of magnesium chloride. High synthesis temperature is favorable to both aragonite fraction and its aspect ratio. High pH is

beneficial to the formation of aragonite. Aging will result in a transformation of aragonite into calcite if calcite exists in the suspension. For the suspension system without calcite and with Mg^{2+}, aging will decrease the needle length and the respect ratio.

Acknowledgment

The authors express their appreciation to David Rothbard for his kind help in the characterization of SEM and to Y. F. Xu., Z. G. Yan, and Q. H. Sun for their help in the experiment.

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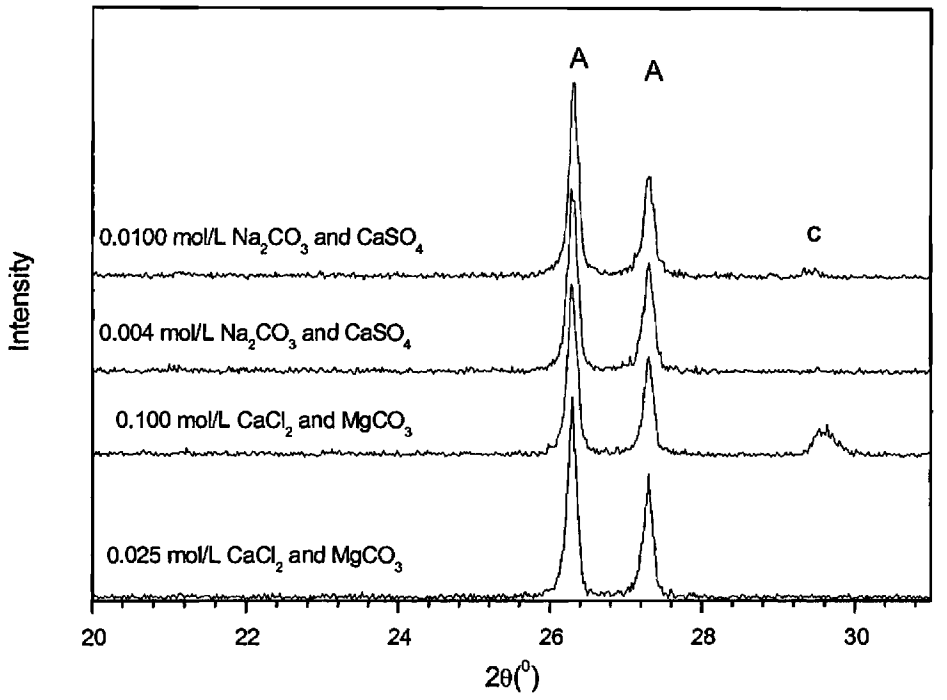

Fig. 1 Effect of $CaCl_2$ concentration on crystal structure of calcium carbonate

A: aragonite; C: calcite

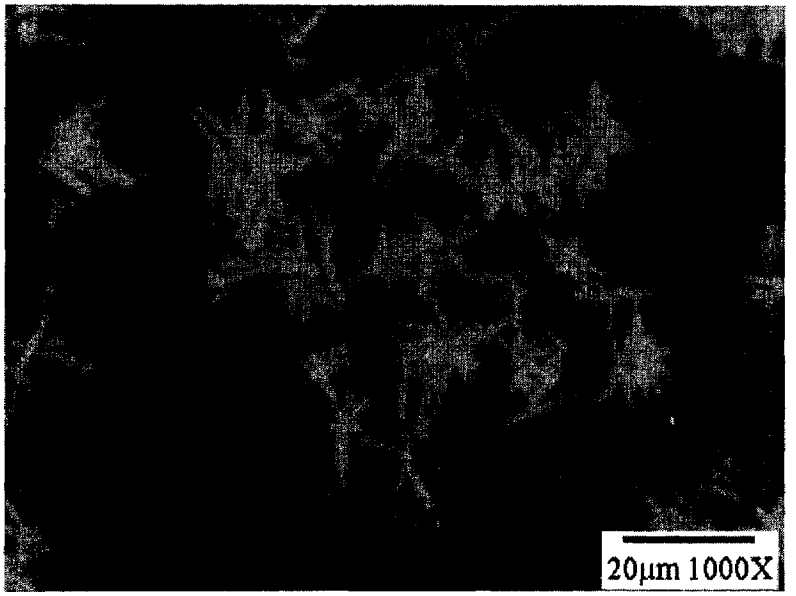

Fig. 2 SEM image of PCC

Prepared from 0.0250 mol/L $CaCl_2$ and $MgCO_3$ suspension at 70^0C

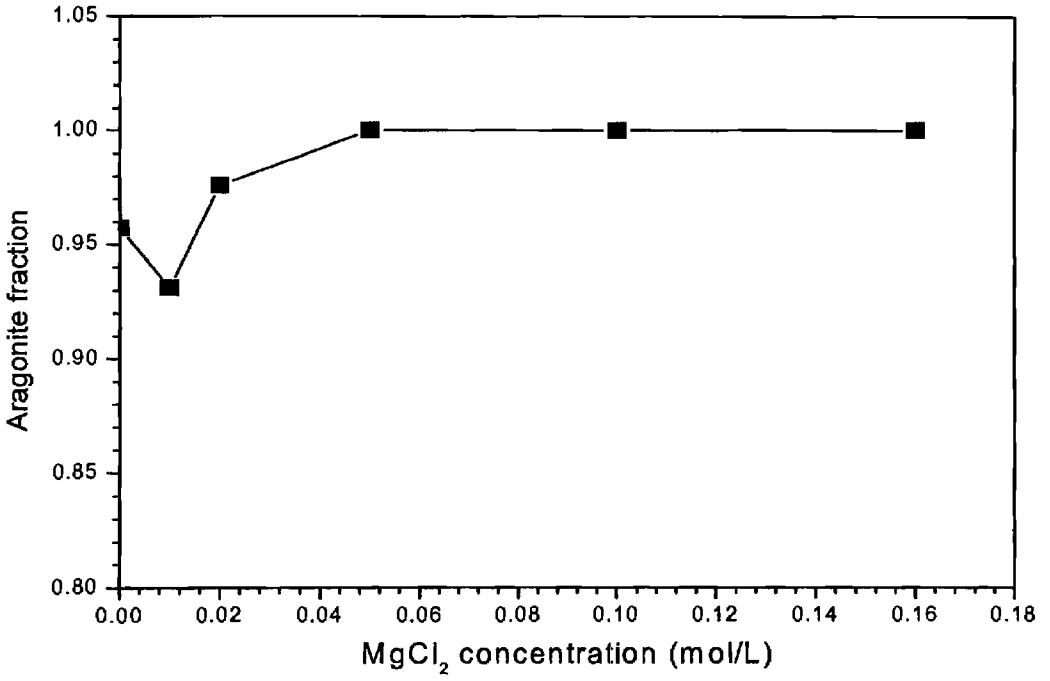

Fig. 3 Effect of $MgCl_2$ on polymorphs of PCC

1.00 mol/L of $CaCl_2$ solution was added to 50 mL of suspension with 2.52 g $MgCO_3$ and different concentrations of $MgCl_2$ at a rate of 0.4 mL/min and at 60°C

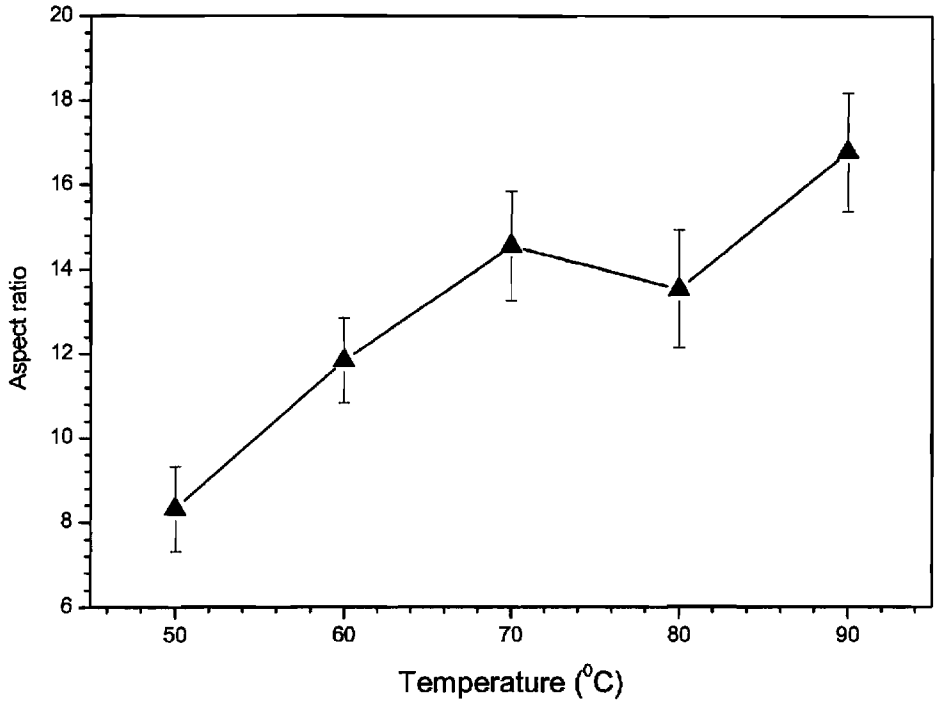

Fig. 4 Effect of temperature on aragonite aspect ratio

1.00 mol/L of $CaCl_2$ solution was added to 50 mL of suspension with 2.52 g $MgCO_3$ and 0.16 mol/L $MgCl_2$ at a rate of 0.4 mL/min

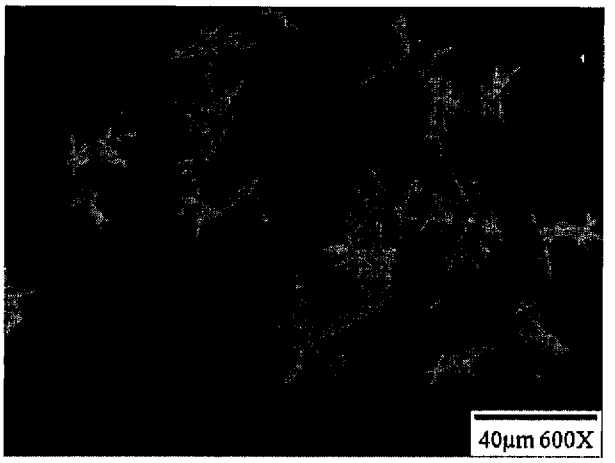

Fig. 5a Prepared at 90°C

Fig. 5b Prepared at 50°C

Fig 5 SEM images of PCC prepared at different temperatures

1.00 mol/L of $CaCl_2$ solution was added to 50 mL of suspension with 2.52 g $MgCO_3$ and 0.16 mol/L $MgCl_2$ at a rate of 0.4 mL/min

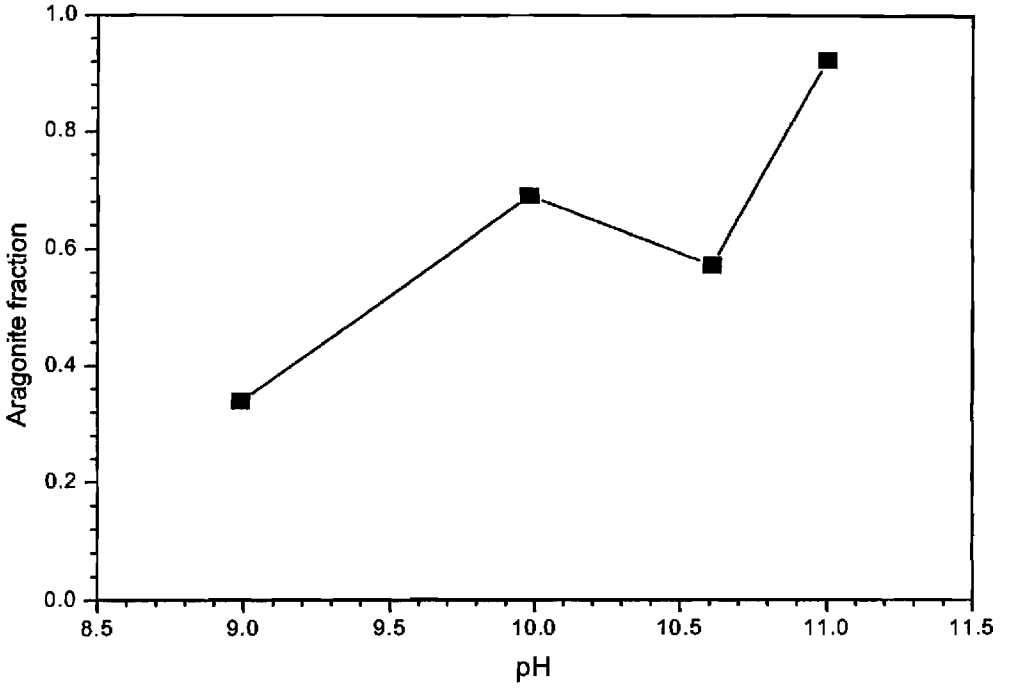

Fig. 6 Effect of suspension pH on polymorphs of PCC

Prepared from $CaCl_2$ solution and $MgCO_3$ suspension at 70^0C

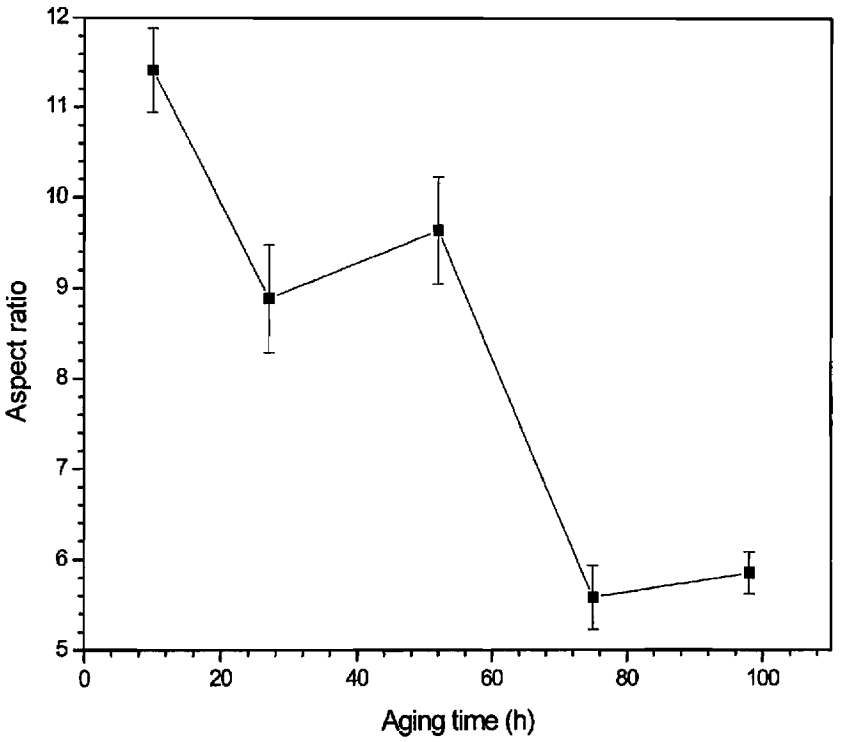

Fig. 7 Effect of aging time on aragonite aspect ratio

1.00 mol/L $CaCl_2$ was added to $MgCO_3$ suspension with 0.16 mol/L $MgCl_2$ at an adding rate of 8 mL/min

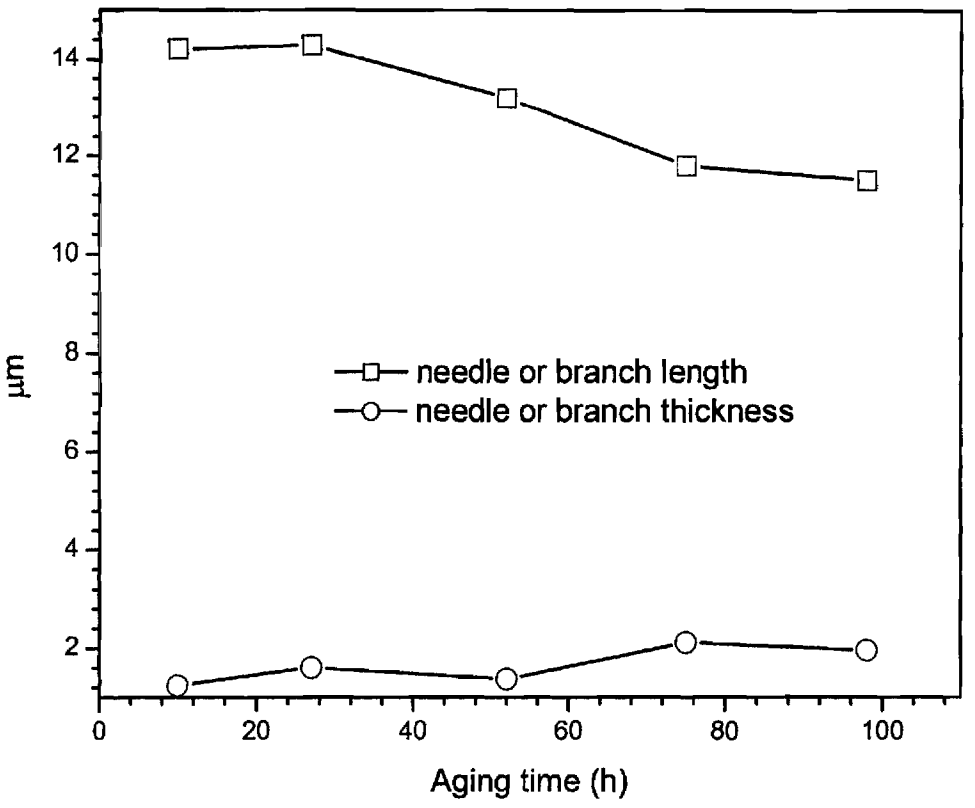

Fig. 8 Effect of aging time on particle size of aragonite

1.00 mol/L $CaCl_2$ was added to $MgCO_3$ suspension with 0.16 mol/L $MgCl_2$ at an adding rate of 8 mL/min

Tables

Table 1 Effect of $CaCl_2$ concentration on polymorphs and aspect ratio of aragonite of calcium carbonate*

$CaCl_2$ Concentration (mol/L)	3.00	1.00	0.100	0.025
Fraction of aragonite	0.197	0.603	0.929	1.00
Aspect ratio	--	11.2	9.97	7.39

*: Prepared from $CaCl_2$ solution and $MgCO_3$ suspension at 70^0C

Table 2 Effect of $MgCl_2$ on crystal size of aragonite*

$MgCl_2$ concentration (mol/L)	0	0.0100	0.0200	0.0500	0.160
Aragonite crystal size (nm)	94.7	118	106	147	304

*: 1.00 mol/L of $CaCl_2$ solution was added to 50 mL of suspension with 2.52 g $MgCO_3$ and different concentrations of $MgCl_2$ at a rate of 0.4 mL/min and at 60^oC